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Investigation of the slow pyrolysis kinetics of olive oil pomace using thermo-gravimetric analysis coupled with mass spectrometry

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ABSTRACT

In this study, slow pyrolysis characteristics of olive oil pomace were investigated by using thermogravimetric analysis coupled with mass spectrometry. The major pyrolysis products identified are H_2 , CH_4 , CO , CO_2 . Their evolution profiles with respect to temperature enable a realistic evaluation of weight loss results. The chemical structure of the olive oil pomace was analyzed using FTIR. Thermogravimetric analysis results have been utilized to determine kinetic parameters by using model fitting (Coats Redfern method), model free (ASTM E698, Flynn–Wall–Ozawa, Friedman methods) and nonlinear regression analysis approaches. Comparative evaluation of the kinetic results indicate that the multivariate regression analysis is an appropriate method to derive kinetic models which give reliable results for the whole temperature range especially in multi-step reactions.

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1. Introduction

Sustainable primary and secondary energy generation from biomass is of utmost importance considering the diminishing availability of fossil fuels and the higher sensibility towards environment preservation from pollutants generated by conventional energy production. Renewable energy derived from biomass reduces reliance on fossil fuels and it does not add new carbon dioxide to the atmosphere. Biomass is a term for all organic material that stems from plants including algae, trees and crops that are susceptible to be converted into energy [1].

Biomass thermolysis has the potential to reduce our dependence on fossil resources by providing alternative fuels and specialty chemicals. Biomass pyrolysis is an important

step in all thermolysis processes such as gasification, liquefaction and combustion [2]. Therefore know-how on pyrolysis products and related kinetics is essential in various energy and chemical production technologies [3]. Pyrolysis is an extremely complex process which goes through a series of reactions and can be influenced primarily by the temperature profile and pressure of the process [4–7]. The differences observed in the pyrolysis behavior of the ligno-cellulosic samples can be attributed primarily to the variations of hemicellulose, lignin and cellulose content of the biomasses under investigation [8].

Thermogravimetric analysis (TGA) is a commonly applied thermo analytical technique in solid-phase thermal degradation studies [9], and it has gained widespread application in thermal studies of biomass pyrolysis [10–15]. TGA coupled

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with mass spectrometry (MS) enables the identification of gaseous species formed during pyrolysis.

Thermogravimetric analysis (TGA) results can be used for kinetic analysis of thermolysis processes. In literature, numerous works describe TGA based kinetics of different materials such as plastics [16–18], inorganics [19–21], urban waste [22–24], fossil fuels [25–27] and biomass [4,28,29] during thermal degradation.

A kinetic model is necessary to predict the thermolysis behavior, to design the necessary equipment and to determine their operation conditions [30].

This paper presents results related to slow pyrolysis of olive oil pomace, the solid residue of olive oil production. This residue includes olives (6–8%), water (20–33%), seeds and pulps (59–74%) depending on the olive oil extraction processes [31]. The annual world production of olive oil is about 3 million tons (statistics from year 2009) yearly and Turkey has ca. 5% share in olive oil production [32]. Slow pyrolysis of olive oil pomace occurs during torrefaction, active carbon formation and char gasification. Hence, the results of this study are applicable to primary and secondary fuel productions from pomace. The produced gas mixture can be converted to synthesis gas which can be catalytically processed to various hydrocarbon products. The solid residue can be utilized as active carbon for adsorption and catalysis.

2. Materials and methods

2.1. Samples

The olive oil pomace used in this study was supplied by the Turkish olive oil producers.

The dried olive oil pomace samples were grinded with a knife mill to get the final size of the sample below 250 μ . Proximate and ultimate analysis results were carried out according to ASTM Standard D5142-04 (TGA 701, LECO). Ultimate analysis was conducted using ASTM Standard D5373-2 (Truspec CHN-S, LECO). The results are summarized in Table 1.

2.2. Experimental apparatus and procedures

Thermogravimetric analysis of olive oil pomace was carried out using Netzsch STA 409 coupled with AELOS 403C QMS

mass spectrometer. A sample mass of 20.0 mg was used in each experiment. Argon was used as a carrier gas with a flow rate of 45 mL/min for pyrolysis experiments. The olive oil pomace samples were heated from 25 °C to 900 °C at four selected heating rates, 1.0, 2.5, 5.0 and 10 °C/min. The sample mass used is high enough to represent the olive pomace sample and low enough to decrease the heat transfer limitation. The applied low heating rates also serve to minimize the impact of heat transfer resistance as much as possible [33].

A portion of the volatiles formed as a result of thermal decomposition was transferred to the ion source of the QMS 403C through a quartz capillary line heated to 250 °C. The m/z ratios of selected products were as follows: m/z 2, 15, 28, 44.

The samples were mixed with KBr for solid FTIR analysis following the standard procedure. Several pomace pellets at various mixture ratios were prepared. Results presented here refer to a pomace KBr 1:30 mass ratios.

2.3. Kinetic analysis

Kinetic analysis is traditionally expected to produce an adequate kinetic description of the process in terms of the reaction model and the Arrhenius parameters, where k_0 is the pre-exponential factor, $f(\alpha)$ a function called the reaction model, E_a the activation energy and R the gas constant. These three components ($f(\alpha)$, E_a , and k_0) are also called the “kinetic triplet” [34].

The rate of heterogeneous solid-state reactions can be described by the Arrhenius equation where t is time, $k(T)$ is the temperature-dependent constant, which describes the dependence of the reaction rate on the extent of reaction, α (Eqn. (1)).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

The extent of reaction, during the thermal degradation can be defined as the ratio of weight loss at time t to the total weight loss corresponding to the degradation process (Eqn. (2)).

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

$$\frac{d\alpha}{dt} = k_0 e^{-\frac{E_a}{RT}} f(\alpha) \quad (3)$$

There are many methods for analyzing non-isothermal solid-state kinetic data from TGA [35,36]. Knowledge of the kinetic parameters, such as the reaction rate and activation energy, is one of the keys to determine reaction mechanisms in solid phase [34].

Kinetic analysis techniques can be classified in three groups as model-fitting (i.e., identification of a kinetic reaction model), iso-conversional (i.e., model-free) and nonlinear regression analysis (Fig. 1).

2.3.1. Model fitting methods

In the model-fitting method, the $f(\alpha)$ term is determined by fitting various reaction models to experimental data.

Table 1 – Characteristics of the olive oil pomace (wt%–dry basis).

Proximate analysis	
Volatile matter	74.26
Fixed carbon	18.95
Ash	6.79
Ultimate analysis	
C	54.72
H	5.24
O	31.97
N	1.14

Subsequently, the $k(T)$ can be evaluated by the chosen form of $f(\alpha)$ [34]. The model-fitting methods are widely used because of their capacity to directly determine the kinetic triplet [34]. In the model fitting technique, the apparent activation energy is assumed to remain constant throughout the whole temperature range. Equation (3) can be transformed into non-isothermal rate expressions describing reaction rates as a function of temperature at a constant heating rate, β :

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} e^{-\frac{E_a}{RT}} f(\alpha) \quad (4)$$

Upon integration

$$g(\alpha) = \frac{k_0}{\beta} \int_0^T e^{-\left(\frac{E_a}{RT}\right)} dT \quad (5)$$

If (E_a/RT) is replaced by x and integration limit is transformed:

$$g(\alpha) = \frac{k_0 E_a}{RT} \int_x^\infty \frac{e^{-x}}{x^2} dx \quad (6)$$

Equation (6) can be written as:

$$g(\alpha) = \frac{k_0 E_a}{RT} p(x) \quad (7)$$

$p(x)$ has no analytical solution but has many approximations [37,38], one of the most popular is the Coats Redfern method [39–42].

2.3.1.1. Coats Redfern method. This method utilizes the asymptotic series expansion for approximating the exponential integral in Eqn. (8), giving

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left[\left(\frac{k_0 R}{E_a \beta}\right) \left(1 - \frac{2RT}{E_a}\right)\right] + \frac{-E_a}{RT} \quad (8)$$

$g(\alpha)$ versus $1/T$, gives E_a and k_0 from the slope and intercept, respectively. The model that gives the best linear fit is selected as the chosen model [43].

2.3.2. Model free methods

Model-free iso-conversional methods allow the activation energy to be estimated as a function of α without choosing the reaction model. The basic assumption of these methods is that the reaction rate for a constant extent of conversion, α , depends only on the temperature [44–47].

2.3.2.1. ASTM E698. Kissinger's method is widely used as a standard ASTM E698 procedure. Its application in pyrolysis may be difficult due to overlapping reactions [48].

The value of activation energy is calculated from a plot of $\ln(\beta/T_m^2)$ against $1000/T_m$ for different heating rates (β), where T_m is the temperature peak of the DTG curve. The equation is as follows:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{k_0 R}{E_a g(\alpha)}\right) - \frac{E_a}{RT_m} \quad (9)$$

E_a can be calculated from the slope of the plot, which is equal to E_a/R .

2.3.2.2. Friedman method. Friedman method is a linear differential method based on iso-conversional technique which assumes the apparent activation energy to remain constant. The Friedman method is in general terms as follows:

$$\frac{d\alpha}{dt} = \beta \left(\frac{d\alpha}{dT}\right) = k_0 e^{-\frac{E_a}{RT}} f(\alpha) \quad (10)$$

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left[\beta \left(\frac{d\alpha}{dT}\right)\right] = \ln[k_0 f(\alpha)] - \frac{E_a}{RT} \quad (11)$$

It is assumed that the conversion function $f(\alpha)$ remains constant, which implies that biomass degradation is independent of temperature and depends only on the rate of mass loss. A plot of $\ln[\beta(d\alpha/dT)]$ versus $1/T$ yields a straight line, the slope of which corresponds to $-E_a/R$ [44].

2.3.2.3. Flynn Ozawa methods (FWO). The Flynn–Wall–Ozawa (FWO) method [45,46,49,50] is an integral iso-conversional technique that assumes the apparent activation energy to remain constant.

Apparent activation energy (E_a) is obtained from a plot of $\ln(\beta_i)$, versus $1000/T_{\alpha,i}$, which represents the linear relation with a given value of conversion at different heating rates.

$$\ln(\beta_i) = \ln\left(\frac{k_0 \alpha E_a}{R g(\alpha)}\right) - 5.331 - 1.052 \frac{E_a}{RT_{\alpha,i}} \quad (12)$$

The subscripts i and α denote the given value of heating rate and the given value of conversion, respectively.

2.3.3. Nonlinear regression analysis

Non-linear regression (NLR) allows a direct fit of the model to the experimental data without a transformation and there are no limitations with respect to the complexity of the model. For this reason, NLR method can be used and iterative procedures can be employed for estimating the reaction model of olive oil pomace.

The calculation of the regression values is carried out by means of a fifth-degree Runge–Kutta procedure using the Prince–Domand embedding formula for automatic optimization of the number of supporting digits [51,52]. To minimize the deviance, least squares (LSQ) method is used and a smooth convergence is ensured.

The calculated curves were obtained by means of NLR. These curves were fitted to the experimental ones and corrected with LSQ. During this procedure quality kinetic parameters of initial values are optimized [52].

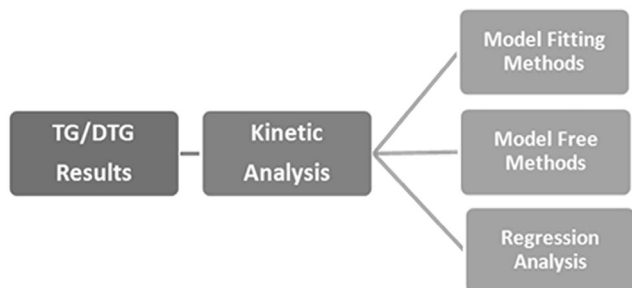


Fig. 1 – Kinetic analysis techniques.

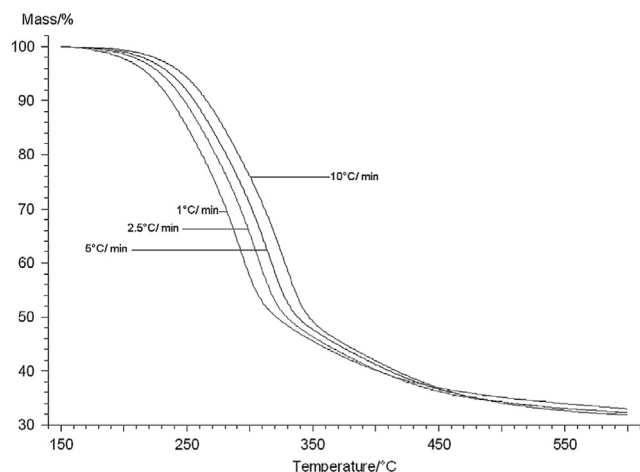


Fig. 2 – Weight versus temperature for various heating rates.

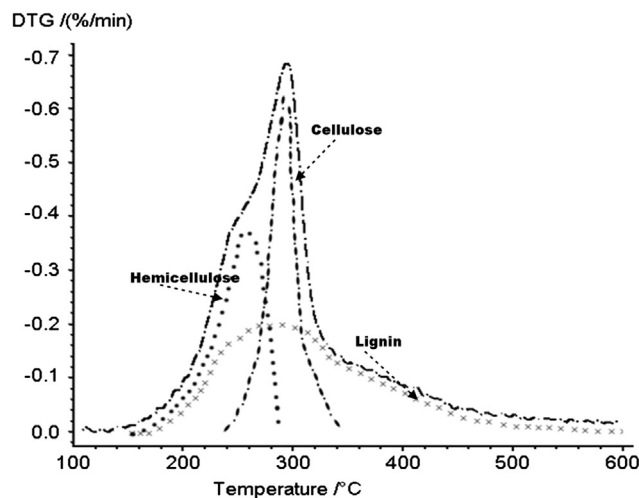


Fig. 4 – Three-component devolatilization model for olive oil pomace at a heating rate of 1 °C/min.

3. Results and discussion

3.1. Thermogravimetry

Olive oil pomace like other biomass sources mainly consists of hemicellulose, cellulose and lignin together with some resins and minerals. Hemicellulose of olive oil pomace begins to decompose after dehydration at lower temperatures ($<150^{\circ}\text{C}$) followed by depolymerization at higher temperatures [49]. Cellulose is decomposed in a way similar to hemicellulose: Decomposition dominates at low temperatures ($<300^{\circ}\text{C}$) and slow heating rates. At higher temperatures, depolymerization and fragmentation are dominant. Inorganic species such as cations, bases, acids and salts can have a major impact on these reactions [53–55]. Lignin—the strengthening component

of the cell wall is thermally more stable than cellulose and hemicellulose and yields more char and a higher fraction of aromatic compounds [53–56]. It is a polymer of hydroxy and methoxy substituted propyl phenol units [57]. At lower temperatures decomposition dominates, while at higher temperatures cracking, reforming, dehydration, condensation, polymerization, oxidation and gasification reactions take place [58–65]. The pyrolysis of cellulosic components primarily occurs around 350°C , while that of lignin covers the whole temperature range ($150\text{--}800^{\circ}\text{C}$) the emphasize being in the high temperature region [2]. Moderate temperatures of around 500°C and short reaction times of up to 2 s are needed to mitigate the secondary vapor phase reactions during biomass pyrolysis [4]. However, the effect of secondary vapor

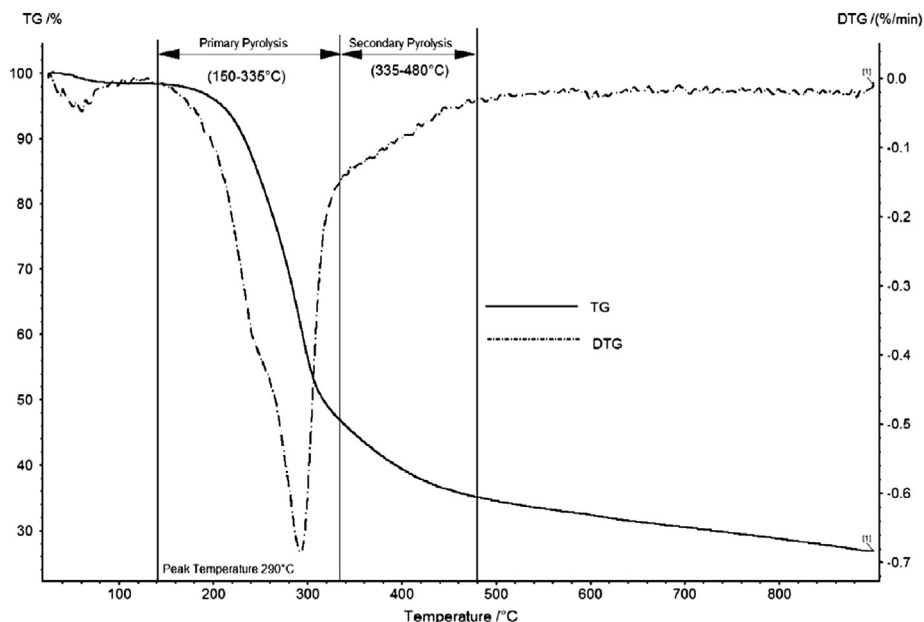


Fig. 3 – Pyrolysis steps at a heating rate of 1 °C/min.

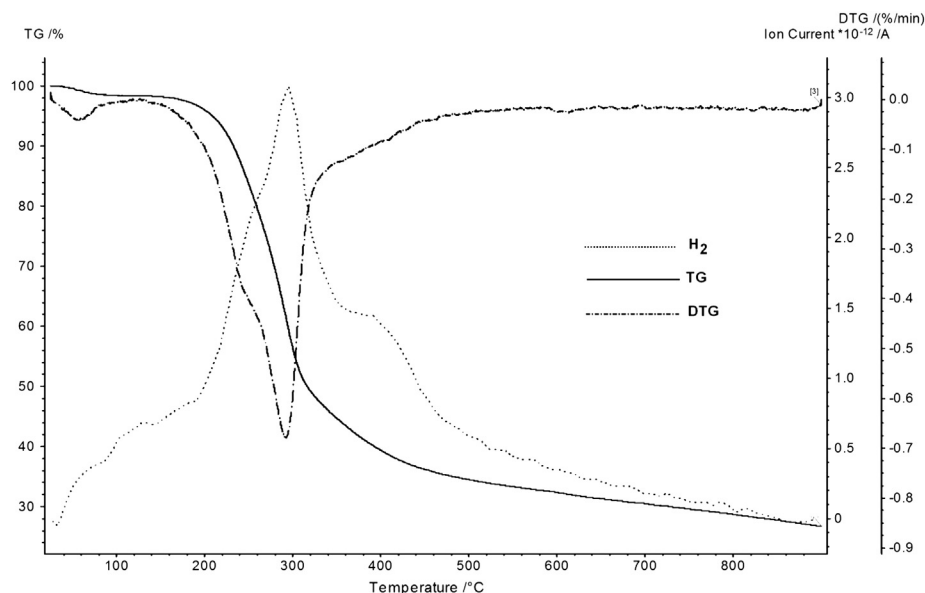


Fig. 5 – Evolution of H_2 (m/z , 2) with temperature increase at a heating rate of 1 °C/min.

phase reactions on pyrolysis product distribution with thermal analysis is poorly known primarily due to the utilized low sample masses.

TGA results of olive oil pomace pyrolysis under argon atmosphere at four different heating rates are given in Fig. 2. As the heating rate increases tenfold from 1 °C to 10 °C the TG and DTG profiles remain almost the same, so are the gas evaluation profiles. The shift is to slightly higher temperatures with increasing heating rates.

Fig. 3 presents the TG-DTG results for 1 °C/min heating rate. For all heating rates, the DTG curve shows two consecutive pyrolysis steps; primary pyrolysis of hemicellulosic and cellulosic components followed by mainly lignin pyrolysis. The main DTG peak corresponds primarily to cellulose

decomposition; the shoulder at lower temperatures can mainly be attributed to hemicellulose devolatilization. Contributions from decomposition of lignin and extractives are visible as wide shoulders on the main devolatilization domain, due to the very broad decomposition range of these components [56].

The devolatilization profiles of hemicellulose, cellulose and lignin for olive oil pomace can be further explained by applying a three-component devolatilization model to the DTG peak [65–68]. Fig. 4 presents the model applied to olive oil pomace pyrolysis at 1 °C/min. The main DTG peak corresponds primarily to cellulose decomposition; the shoulder at lower temperatures can mainly be attributed to hemicellulose devolatilization. Contributions from decomposition of lignin

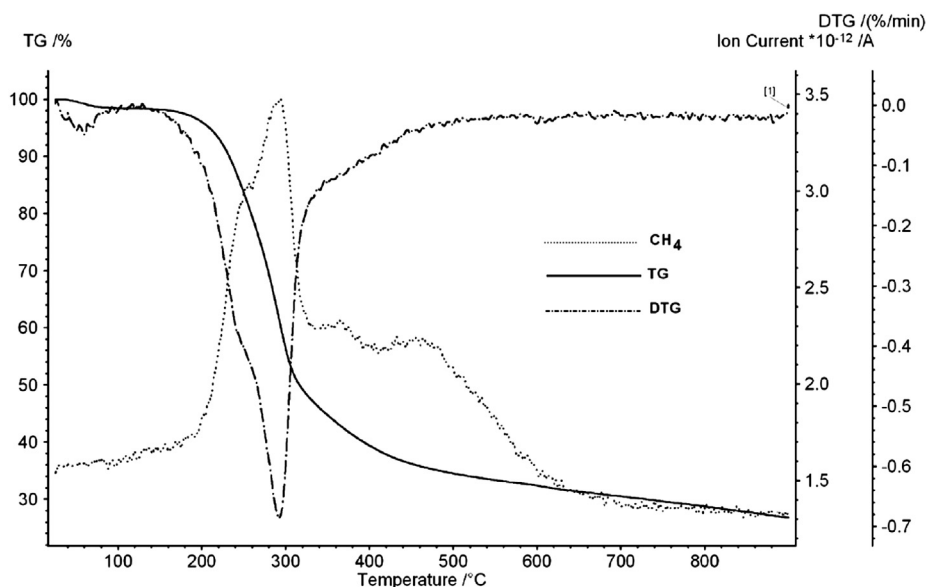


Fig. 6 – Evolution of CH_4 (m/z , 15) with temperature increase at a heating rate of 1 °C/min.

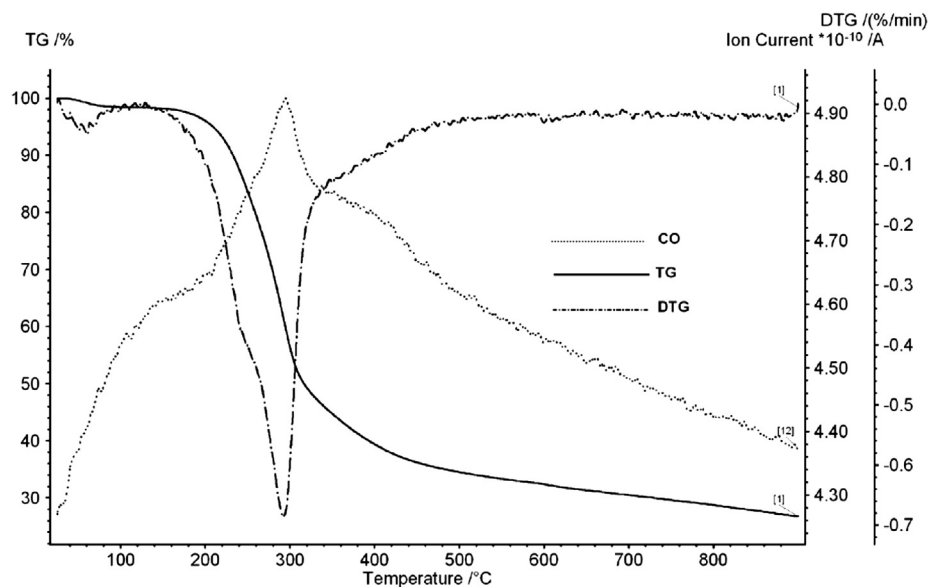


Fig. 7 – Evolution of CO (m/z , 28) with temperature increase at a heating rate of 1 °C/min.

and extractives are visible as wide shoulders on the main devolatilization domain [65–68].

As Fig. 4 indicates hemicellulose of olive oil pomace is easily degraded, and its pyrolysis occurs around 150–295 °C. The pyrolysis of cellulose mainly happens around 245–335 °C, while that of lignin covers the whole temperature range (150–480 °C).

Hence, the first lower temperature step is associated with the decomposition of hemicellulosic and cellulosic materials; this step also contains part of the low temperature lignin decomposition products. The global maximum degradation rates are indicated by the DTG peaks. The second higher temperature decomposition step is less pronounced than the

lower temperature step and indicates primarily lignin pyrolysis.

During the primary pyrolysis of olive oil pomace thermal cracking of chemical bonds in the individual constituents of olive oil pomace, which are mainly cellulose, hemicelluloses and part of the lignin, takes place and permanent gas species (e.g. CO₂, CO, CH₄) and condensable species at ambient conditions (several organic compounds and water) are evolved.

The secondary pyrolysis of olive oil pomace takes place in the range of 335–480 °C along with the formation of a solid char residue. During the secondary pyrolysis, serial and parallel reactions take place, occurring either heterogeneously or homogeneously, as for example cracking, reforming,

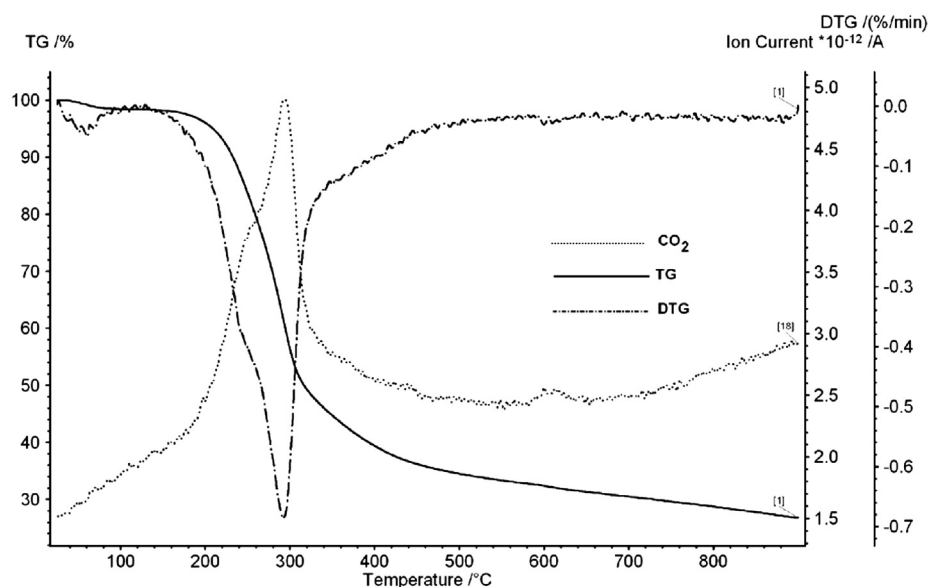


Fig. 8 – Evolution of CO₂ (m/z , 44) with temperature increase at a heating rate of 1 °C/min.

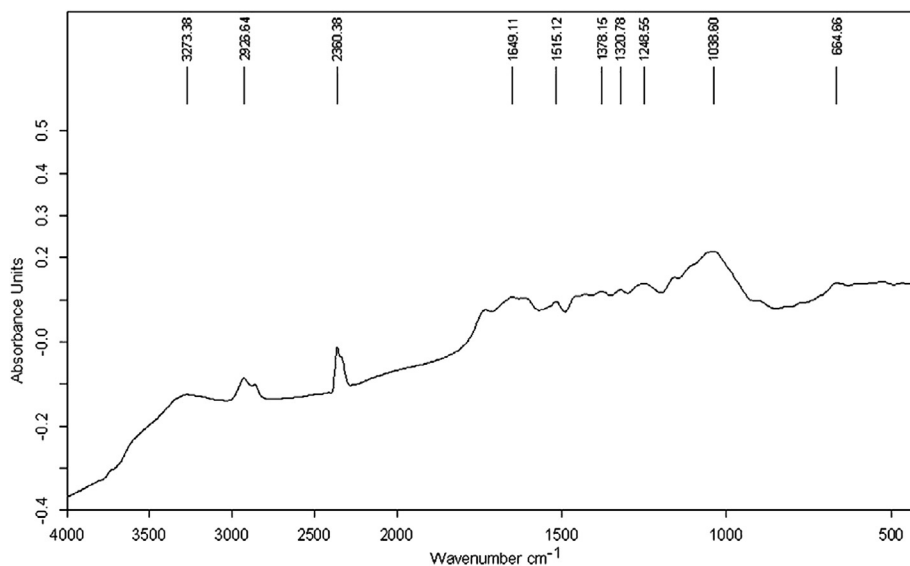


Fig. 9 – The FTIR spectrum of the olive oil pomace.

dehydration, condensation, polymerization, oxidation and gasification reactions [58–65].

3.2. Mass spectrometry

Combining TGA with gas-analytical techniques enhances the possibilities for correctly interpreting the mechanism of thermally induced reactions, which involve the formation of gaseous species. It offers the ability to solve a wide range of problems and applications based on the determination of the composition of complex gas mixtures produced from the decomposition of different types of sample.

Numerical results presented here refer to 1 °C/min heating rate. The peak temperatures of the evolved gases increase with increasing heating rates. The maximum difference has been observed with hydrogen. A tenfold increase of the heating rate from 1 to 10 °C/min increased the peak temperature 15%.

The evolution of H₂ shows a first major peak at 305 °C and a shoulder referring to a second peak around 400 °C (Fig. 5). The release of H₂ at higher temperature is due to the cracking of heavy hydrocarbons (secondary pyrolysis), while the release at the lower temperature is due to primary pyrolysis [69]. Hence, both primary and secondary pyrolysis reactions produce hydrogen.

CH₄ evolution occurs throughout the whole pyrolysis temperature range (Fig. 6). In the lower temperature region the shoulder indicates hemicellulosic CH₄ followed by the peaking CH₄ evolution primarily from cellulosic components. CH₄ is mainly produced by the cracking of methoxyl groups of the lignin at higher temperatures [56,69].

The evolution of CO commences at around 245 °C, reaches its maximum at 335 °C, and then it is prolonged (Fig. 7). The release of CO and CO₂ between 245 and 335 °C is probably due to the breaking of C–C and C–O bonds which essentially originate from hemi-cellulose and cellulose and the release of

CO at higher temperatures is due to lignin, possibly through the release of COOH groups and the breaking of C–O groups [62]. Cellulose gives the highest CO yield, due to its high carbonyl content [56,69,70].

CO₂ release is mainly due to the primary pyrolysis, while secondary pyrolysis is the main source for the release of CO and CH₄ (Fig. 8). Hemicellulose displays the highest CO₂ yield because of the higher carboxyl content [56,69,70].

3.3. FTIR analysis

The FTIR spectrum of the olive oil pomace is shown in Fig. 9 olive oil pomace contains primarily alkenes, esters, aromatics, ketones and alcohols with different oxygen-containing functional groups [56]. The FTIR signals with the assigned possible compounds and the typical functional groups are listed in Table 2 for a reference [2,71,72].

Table 2 – The main functional groups of olive oil pomace.

Wave number (cm ⁻¹)	Functional groups	Compounds
3273	O–H stretch	Acid; ether linkage
2927	C–H stretch	Alkyl
2360		Linked water
1649	CH ₂ bend	Alkanes
1515	O–H bend	Acid
1378	C–H bend	Alkyl
1321		Xylan
1249	C–O–C stretch vibration	Pyranose ring skeletal
1039	C–O stretch	Hydroxyl group
665	C–H bend	β-D-Xylose

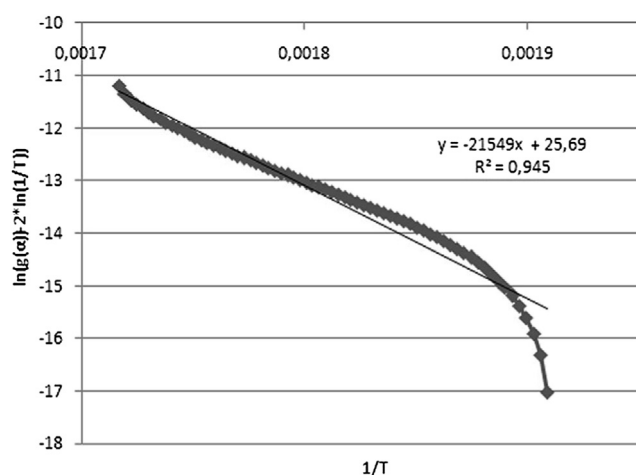


Fig. 10 – A plot of $\ln(g(\alpha)) - 2\ln(1/T)$ versus $1/T$ for pyrolysis kinetics of olive oil pomace between 250 °C–310 °C.

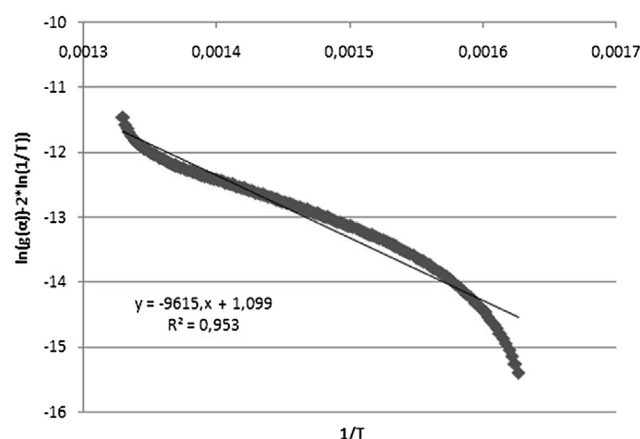


Fig. 12 – Phase 2: A plot of $\ln(g(\alpha)) - 2\ln(1/T)$ versus $1/T$ for pyrolysis kinetics of olive oil pomace between 335 °C–480 °C.

3.4. Kinetic results

3.4.1. Model fitting method

The activation energy (E_a) and the pre-exponential factor (k_0) were obtained assuming the olive oil pomace decomposition as a first order reaction with the Coats Redfern method utilizing the TG data at 1 °C/min.

The first temperature range of interest is chosen as 250 °C–310 °C based on the DTG results. The low temperature limit corresponds to the maximum decomposition rate of hemicellulose. The temperature range includes the maximum decomposition rate of cellulose at 292 °C and ends when cellulose decomposition is completed (Fig. 4). Fig. 10 shows a plot of $\ln(g(\alpha)) - 2\ln(1/T)$ versus $1/T$ for pyrolysis kinetics of olive oil pomace between 250 °C–310 °C. The results indicate an activation energy of 179.15 kJ/mol and a pre-exponential factor of $3.09 \times 10^{12} \text{ s}^{-1}$.

In the second olive oil pomace pyrolysis kinetics calculation approach, two consecutive temperature ranges which

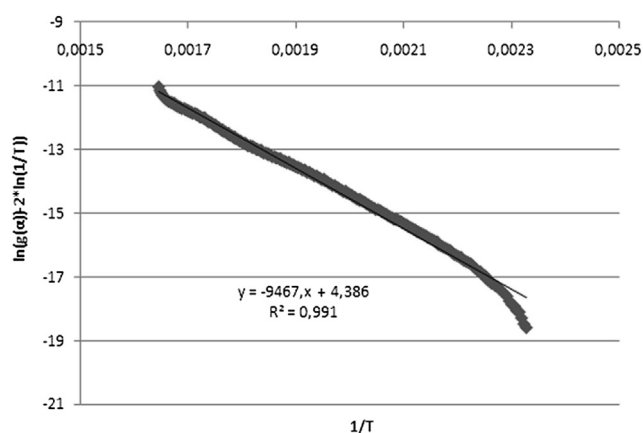


Fig. 11 – Phase I: A plot of $\ln(g(\alpha)) - 2\ln(1/T)$ versus $1/T$ for pyrolysis kinetics of olive oil pomace between 150 °C–335 °C.

correspond to primary and secondary pyrolysis phases were selected. Figs. 11 and 12 show the associated kinetic calculation results. The lower temperature range covers 150 °C–335 °C (phase I) while the higher temperature range is between 335 °C–480 °C (phase II). The values of the activation energy and pre-exponential factors were calculated as 78.70 kJ/mol and 79.93 kJ/mol and a pre-exponential factor of $7.60 \times 10^2 \text{ s}^{-1}$ and $2.87 \times 10^2 \text{ s}^{-1}$ for pyrolysis phases I and II, respectively.

3.4.2. Model free methods

A series of non-isothermal TG measurements with different heating rates result in a set of data which enables the collection of data for the same degree of conversion (α) at different temperatures [34]. Based on this idea, the activation energy (E_a) and pre-exponential factor (k_0) are obtained using Kissinger, Friedman and Flynn–Wall–Ozawa (FWO) methods. The data (β , α , T) for kinetic calculations explained in Section 2.3 are taken from the TG curves.

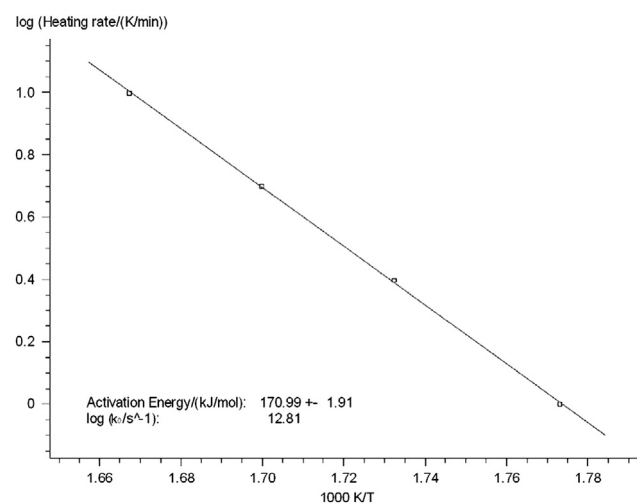


Fig. 13 – A plot of $\log(\beta)$ against $1000 K/T_m$ at four different heating rates (1, 2.5, 5, 10 °C/min).

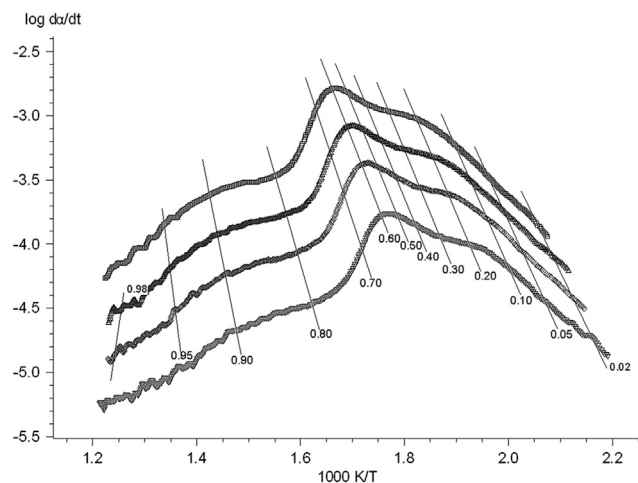


Fig. 14 – The plot of $\log(d\alpha/dt)$ against 1000 K/T at four different heating rates (1, 2.5, 5, 10 °C).

3.4.2.1. ASTM 698. Kinetic parameters are obtained from TG curves at four different heating rates (1, 2.5, 5, 10 °C per minute) using ASTM E698. The slopes and the intercepts of the straight lines (Fig. 13) give the activation energy and the pre-exponential factor as $170.99\text{ kJ mol}^{-1}$ and $6.46 \times 10^{12}\text{ s}^{-1}$, respectively.

3.4.2.2. Friedman analysis. The graphs $\ln(d\alpha/dt)$ versus $1000/T$ yield straight lines for each conversion α with slopes directly proportional to the reaction activation energy (E_a) (Fig. 14).

The activation energy and pre-exponential factors remain almost constant around 173 kJ/mol and $1.65 \times 10^{14}\text{ s}^{-1}$ in the conversion range of $0.05 \leq \alpha \leq 0.65$. An increase of these values is observed at higher conversions. Fig. 15 shows these lines at different α and the calculated results using both Eqs. (10) and (11). The upper and lower curves in Fig. 15 indicate the statistical errors associated with Friedman analysis for pre-exponential factors and activation energies, respectively, at

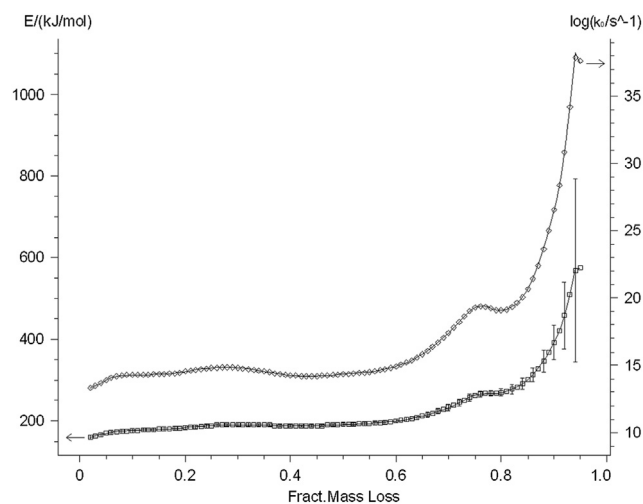


Fig. 15 – Friedman analysis–energy plot, β “1, 2.5, 5 and 10 °C/min”.

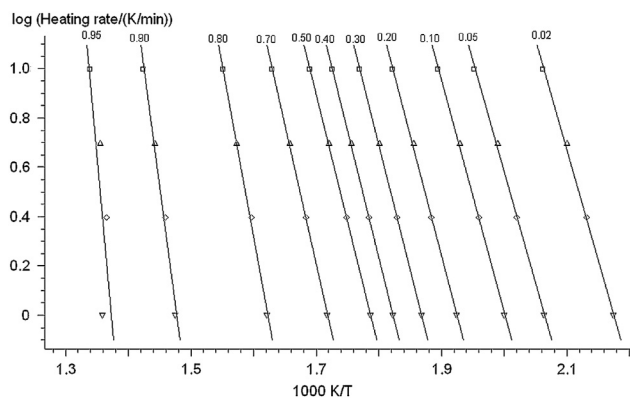


Fig. 16 – The plots of $\log(\beta)$ against 1000 K/T at four different heating rates (1, 2.5, 5, 10 °C).

fractional mass losses. Our TG results suggest that results are acceptable up to 0.7 conversions. Beyond this range ($\alpha \geq 0.70$), these values start to fluctuate.

3.4.2.3. Flynn–Wall–Ozawa. The graphs $\ln(\beta)$ versus $1/T$ and $\ln(d\alpha/dt)$ versus $1/T$ both show straight lines (Fig. 16) with slopes directly proportional to the reaction activation energy (E_a). The values of the activation energy and pre-exponential factors are increasing slowly in conversion range of $0.05 \leq \alpha \leq 0.65$, and beyond this range ($\alpha \geq 0.65$), both kinetic values increase rapidly. The upper and lower curves in Fig. 17 indicate the statistical errors associated with Flynn–Wall–Ozawa analysis for pre-exponential factors and activation energies, respectively, at fractional mass losses.

3.4.3. Non-linear regression analysis

Multivariate non-linear regression (NLR) program was applied to determine the mechanism and the corresponding kinetic parameters of slow pyrolysis. Simulations were performed by using “Netzsch Thermokinetics: A Software Module for the Kinetic analysis of Thermal Measurements”. The non-

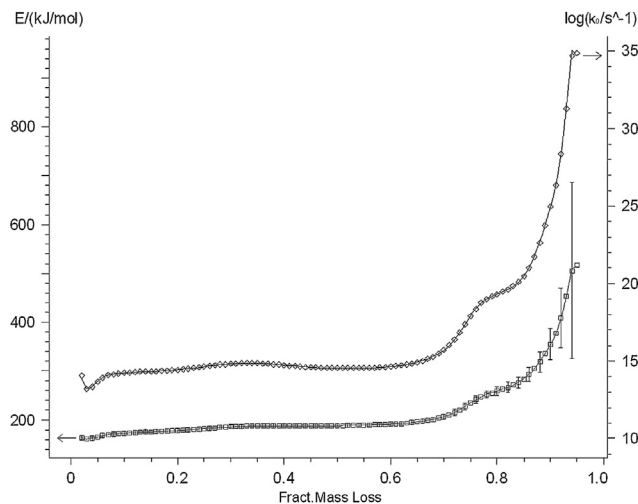


Fig. 17 – FWO analysis–energy plot, β “1, 2.5, 5 and 10 °C/min”.

Table 3 – The four steps kinetic model.

Reaction No	Type
1	3-dim. diffusion Janders type
2	n-th order
3	n-th order
4	n-th order
Model $A \xrightarrow{1} B \xrightarrow{2} C \xrightarrow{3} D \xrightarrow{4} E$	

isothermal data recorded at four heating rates were brought together during analysis and the relevant differential equations of the reaction rates were numerically solved and the kinetic parameters were iteratively optimized. The calculated curves were obtained by means of non-linear regression. These curves were fitted to the experimental ones and corrected with least square method. During this procedure initial values are optimized in order to get high fitting quality kinetic parameters. The calculations were performed for conversions of $0.05 \leq \alpha \leq 0.70$. The proposed four steps reaction model is given in Table 3. For all cases the reaction order is changed between 0.5–2.5 to find the best fit.

Fig. 18 shows the fit of the values calculated with non-linear regression analysis to the experimental TG data at the four selected heating rates. The correlation coefficient is 0.9977.

Table 4 summarizes the activation energy and pre-exponential factor results for the before mentioned kinetic methods along with the non-linear regression method.

4. Concluding remarks

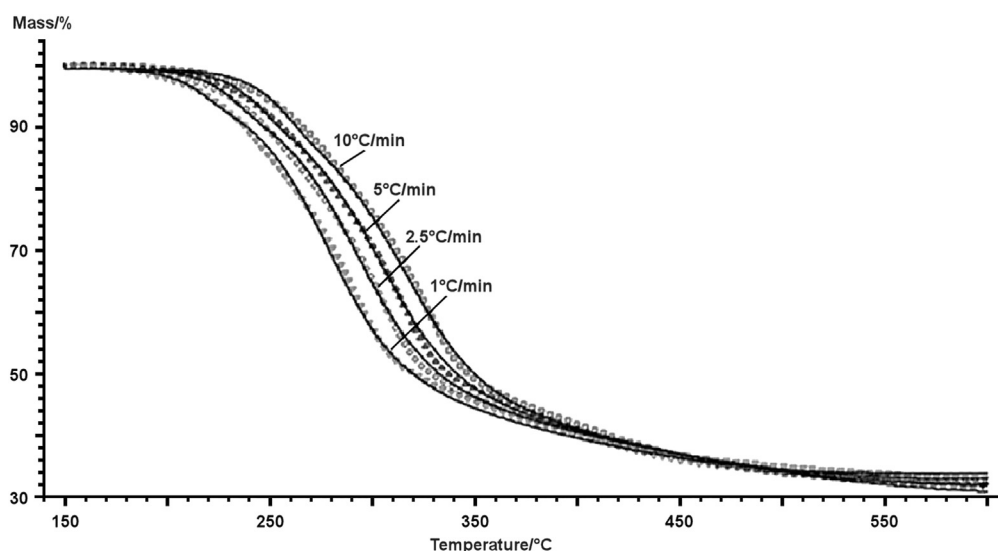
Investigation of the slow pyrolysis kinetics of olive oil pomace using thermo-gravimetric analysis coupled with mass spectrometry enables co-current determination of the pyrolysis based weight loss and the evolution of selected gaseous

Table 4 – Non-linear regression analysis results.

Reaction	Parameter	Optimum value
$A \xrightarrow{1} B$	$\log k_0 \text{ 1/s}^{-1}$	10.68
	$E_{a1} \text{ kJ/mol}$	155.10
$B \xrightarrow{2} C$	$\log k_0 \text{ 2/s}^{-1}$	9.90
	$E_{a2} \text{ kJ/mol}$	170.31
$C \xrightarrow{3} D$	React.ord. 2	2.36
	$\log k_0 \text{ 3/s}^{-1}$	20.41
$D \xrightarrow{4} E$	$E_{a3} \text{ kJ/mol}$	263.45
	React.ord. 3	0.75
	$\log k_0 \text{ 4/s}^{-1}$	9.08
	$E_{a4} \text{ kJ/mol}$	130.57
	React.ord. 4	1.40

products as a function of temperature. Both weight loss and gas evolution (in this case H_2 , CH_4 , CO , CO_2) profiles are useful in the interpretation of the kinetic results. In other words, TGA/MS experiments can be designed to understand the kinetics of thermolysis processes.

Pyrolysis reactions are not simple one-step processes; they constitute a combination of serial and parallel steps. Hence, kinetic parameters change during the course of the reactions. The most applied kinetic method in literature is the Coats Redfern method. Our studies indicate that the temperature range of interest is of utmost importance for the results of this method. The activation energy and pre-exponential factor results with Coats Redfern based on maximum conversion are in good agreement with the model free methods. Kinetic results obtained with Coats Redfern for two wide pyrolysis temperature ranges are much lower. The results of the chosen four steps kinetic model are also in the range of the former results. Only model free methods estimate the potential model(s) according to which the reactions occur. All approaches give information about the pyrolysis kinetics. One should first of all comparatively evaluate them and then the method most suitable for the research purpose should be selected.

**Fig. 18 – The calculated values to the experimental data at the four selected heating rates.**

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Nomenclature

α	the given value of conversion
E_a	apparent activation energy (kJ mol^{-1})
$f(\alpha)$	reaction model (function expressing the dependence of the reaction rate on the conversion)
$g(\alpha)$	integrated reaction model
i	denote the given value of heating rate
k_0	pre-exponential factor (s^{-1})
$k(T)$	temperature-dependent rate constant (s^{-1})
$p(x)$	temperature integral
R	universal gas constant ($8.3144 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$)
t	time (s)
T	temperature (K)
x	E_a/RT

Greek letters

α	conversion
β	heating rate ($^{\circ}\text{C/s}$)

REFERENCES

- [1] McKendry P. Energy production from biomass (part 1): overview of biomass. *Bioresource Technol* 2002;83(1):37–46.
- [2] Yang HP, Yan R, Chen HP, Lee DH, Zheng CG. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007;86(12–13):1781–8.
- [3] Seo DK, Park SS, Hwang J, Yu TU. Study of the pyrolysis of biomass using thermo-gravimetric analysis (TGA) and concentration measurements of the evolved species. *J Anal Appl Pyrol* 2010;89(1):66–73.
- [4] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* 2012;38:68–94.
- [5] Manya JJ, Velo E, Puigjaner L. Kinetics of biomass pyrolysis: a reformulated three-parallel-reactions model. *Ind Eng Chem Res* 2003;42(3):434–41.
- [6] Varhegyi G, Antal MJ, Jakab E, Szabo P. Kinetic modeling of biomass pyrolysis. *J Anal Appl Pyrol* 1997;42(1):73–87.
- [7] Raveendran K, Ganesh A, Khilar KC. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel* 1995;74(12):1812–22.
- [8] Sanchez-Silva L, Lopez-Gonzalez D, Villasenor J, Sanchez P, Valverde JL. Thermogravimetric-mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis. *Bioresource Technol* 2012;109:163–72.
- [9] Ninan KN. Kinetics of solid-state thermal-decomposition reactions. *J Therm Anal* 1989;35(4):1267–78.
- [10] Teng HS, Lin HC, Ho JA. Thermogravimetric analysis on global mass loss kinetics of rice hull pyrolysis. *Ind Eng Chem Res* 1997;36(9):3974–7.
- [11] Stenseng M, Jensen A, Dam-Johansen K. Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry. *J Anal Appl Pyrol* 2001;58-59(1):765–80.
- [12] Meszaros E, Varhegyi G, Jakab E. Thermogravimetric and reaction kinetic analysis of biomass samples from an energy plantation. *Energ Fuel* 2004;18(2):497–507.
- [13] Zhang XD, Xu M, Sun RF, Sun L. Study on biomass pyrolysis kinetics. *J Eng Gas Turbines Power-transactions Asme* 2006;128(3):493–6.
- [14] Branca C, Iannace A, Di Blasi C. Devolatilization and combustion kinetics of *Quercus cerris* bark. *Energ Fuel* 2007;21(2):1078–84.
- [15] d’Almeida ALFS, Barreto DW, Calado V, d’Almeida JRM. Thermal analysis of less common lignocellulose fibers. *J Therm Anal Calorim* 2008;91(2):405–8.
- [16] Garcia AN, Marcilla A, Font R. Thermogravimetric kinetic-study of the pyrolysis of municipal solid-waste. *Thermochim Acta* 1995;254(4):277–304.
- [17] Zhou LM, Wang YP, Huang QW, Cai JQ. Thermogravimetric characteristics and kinetic of plastic and biomass blends co-pyrolysis. *Fuel Proc Tech* 2006;87(11):963–9.
- [18] Menad N, Bjorkman B, Allain EG. Combustion of plastics contained in electric and electronic scrap. *Resour Conservation Recycling* 1998;24(1):65–85.
- [19] Gunasekaran S, Natarajan RK, Kala A. FTIR spectra and mechanical strength analysis of some selected rubber derivatives. *Spectrochimica Acta Part A-Molecular Biomol Spectrosc* 2007;68(2):323–30.
- [20] Aigbodion AI, Okieimen FE, Obazee EO, Bakare IO. Utilisation of maleinized rubber seed oil and its alkyd resin as binders in water-borne coatings. *Prog Org Coat* 2003;46(1):28–31.
- [21] Grammelis P, Basinas P, Malliopoulou A, Sakellariopoulos G. Pyrolysis kinetics and combustion characteristics of waste recovered fuels. *Fuel* 2009;88(1):195–205.
- [22] Urban DL, Antal MJ. Study of the kinetics of sewage-sludge pyrolysis using Dsc and Tga. *Fuel* 1982;61(9):799–806.
- [23] Pouet MF, Grasmick A. Urban waste-water treatment by electrocoagulation and flotation. *Water Sci Technol* 1995;31(3–4):275–83.
- [24] Haastrup P, Maniezzo V, Mattarelli M, Rinaldi FM, Mendes I, Paruccini M. A decision support system for urban waste management. *Eur J Oper Res* 1998;109(2):330–41.
- [25] Samanli S, Cuhadaroglu D, Ipek H, Ucbas Y. The investigation of grinding kinetics of power plant solid fossil fuel in ball mill. *Fuel* 2010;89(3):703–7.
- [26] Radetzki M. What will happen to the producer prices for fossil fuels if Kyoto is implemented? *Energy Policy* 2002;30(5):357–69.
- [27] Shafiee S, Topal E. When will fossil fuel reserves be diminished? *Energy Policy* 2009;37(1):181–9.
- [28] Babu SP. Thermal gasification of biomass technology developments: end of task report for 1992 to 1994. *Biomass Bioenergy* 1995;9(1–5):271–85.
- [29] Song T, Wu JH, Shen LH, Xiao J. Experimental investigation on hydrogen production from biomass gasification in interconnected fluidized beds. *Biomass Bioenergy* 2012;36:258–67.
- [30] Koufopoulos CA, Papayannakos N, Maschio G, Lucchesi A. Modeling of the pyrolysis of biomass particles—studies on kinetics, thermal and heat-transfer effects. *Can J Chem Eng* 1991;69(4):907–15.
- [31] Nuhoglu Y, Malkoc E. Thermodynamic and kinetic studies for environmentally friendly Ni(II) biosorption using waste pomace of olive oil factory. *Bioresource Technol* 2009;100(8):2375–80.
- [32] www.internationaloliveoil.org; August 2012.

- [33] Nowicki L, Markowski M. Kinetic analysis of thermogravimetric data collected from bigger samples. *Chem Process Eng-inz* 2012;33:85–94.
- [34] Ramajo-Escalera B, Espina A, Garcia JR, Sosa-Arnan JH, Nebra SA. Model-free kinetics applied to sugarcane bagasse combustion. *Thermochim Acta* 2006;448(2):111–6.
- [35] Simon P. Isoconversional methods—fundamentals, meaning and application. *J Therm Anal Calorim* 2004;76(1):123–32.
- [36] Sbirrazzuoli N, Vincent L, Mija A, Guigo N. Integral, differential and advanced isoconversional methods complex mechanisms and isothermal predicted conversion-time curves. *Chemometr Intell Lab* 2009;96(2):219–26.
- [37] Chen HJ, Lai KM, Lin YC. Methods for determining the kinetic parameters from nonisothermal thermogravimetry: a comparison of reliability. *J Chem Eng Jpn* 2004;37(9):1172–8.
- [38] Agrawal RK, Sivasubramanian MS. Integral approximations for nonisothermal kinetics. *Aiche J* 1987;33(7):1212–4.
- [39] Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. *Nature* 1964;201(491):68–9.
- [40] Gao W, Chen K, Xiang Z, Yang F, Zeng J, Li J, et al. Kinetic study on pyrolysis of tobacco residues from the cigarette industry. *Ind Crops Prod* 2013;44:152–7.
- [41] Galwey AK. Perennial problems and promising prospects in the kinetic analysis of nonisothermal rate data. *Thermochim Acta* 2003;407:93–103.
- [42] House JE. Principles of chemical kinetics. 2nd ed. San Diego: Academic Press; 2007.
- [43] Ebrahimi-Kahrizangi R, Abbasi MH. Evaluation of reliability of Coats-Redfern method for kinetic analysis of non-isothermal TGA. *T Nonfer Metal Soc* 2008;18(1):217–21.
- [44] Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to phenolic plastic. *J Polym Sci Pol Sym* 1964;6:183–95.
- [45] Ozawa T. A new method of analyzing thermogravimetric data. *Bull Chem Soc Jpn* 1965;38(11):1881–6.
- [46] Flynn JH, Wall LA. General treatment of thermogravimetry of polymers. *J Res Nbs a Phys Ch* 1966;70(6):487–523.
- [47] Vyazovkin S, Dollimore D. Linear and nonlinear procedures in isoconversional computations of the activation energy of nonisothermal reactions in solids. *J Chem Inf Comp Sci* 1996;36(1):42–5.
- [48] Stolarek P, Ledakowicz S. Pyrolysis kinetics of chitin by non-isothermal thermogravimetry. *Thermochim Acta* 2005;433(1–2):200–8.
- [49] White JE, Catallo WJ, Legendre BL. Biomass pyrolysis kinetics: a comparative critical review with relevant agricultural residue case studies. *J Anal Appl Pyrol* 2011;91(1):1–33.
- [50] Flynn JH, Wall LA. A quick direct method for determination of activation energy from thermogravimetric data. *J Polym Sci Pol Lett* 1966;4(5):323–8.
- [51] Slovak V, Susak P. Pitch pyrolysis kinetics from single TG curve. *J Anal Appl Pyrol* 2004;72(2):249–52.
- [52] Shen XQ, Li ZJ, Zhang HY, Zhou YF, Liu K, Wu QA, et al. Mechanism and kinetics of thermal decomposition of 5-benzylsulfanyl-2-amino-1,3,4-thiadiazole. *Thermochim Acta* 2005;428(1–2):77–81.
- [53] Shafizadeh F. Introduction to pyrolysis of biomass. *J Anal Appl Pyrol* 1982;3(4):283–305.
- [54] Pan WP, Richards GN. Influence of metal-ions on volatile products of pyrolysis of wood. *J Anal Appl Pyrol* 1989;16(2):117–26.
- [55] Scott DS, Paterson L, Piskorz J, Radlein D. Pretreatment of poplar wood for fast pyrolysis: rate of cation removal. *J Anal Appl Pyrol* 2001;57(2):169–76.
- [56] Demirbas A. Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Convers Manag* 2000;41(6):633–46.
- [57] Alen R, Kuoppala E, Oesch P. Formation of the main degradation compound groups from wood and its components during pyrolysis. *J Anal Appl Pyrol* 1996;36(2):137–48.
- [58] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuel* 2006;20(3):848–89.
- [59] Thunman H, Niklasson F, Johnsson F, Leckner B. Composition of volatile gases and thermochemical properties of wood for modeling of fixed or fluidized beds. *Energy Fuel* 2001;15(6):1488–97.
- [60] Gomez-Barea A, Leckner B. Modeling of biomass gasification in fluidized bed. *Prog Energy Combust* 2010;36(4):444–509.
- [61] Kersten SRA, Wang XQ, Prins W, van Swaaij WPM. Biomass pyrolysis in a fluidized bed reactor. Part 1: literature review and model simulations. *Ind Eng Chem Res* 2005;44(23):8773–85.
- [62] Roberts AF. Review of kinetics data for pyrolysis of wood and related substances. *Combust Flame* 1970;14(1–3):261–72.
- [63] Antal MJ. Effects of reactor severity on the gas-phase pyrolysis of cellulose-derived and kraft lignin-derived volatile matter. *Ind Eng Chem Prod Rd* 1983;22(2):366–75.
- [64] Ranzi E, Cuoci A, Faravelli T, Frassoldati A, Migliavacca G, Pierucci S, et al. Chemical kinetics of biomass pyrolysis. *Energy Fuel* 2008;22(6):4292–300.
- [65] Di Blasi C. Modeling chemical and physical processes of wood and biomass pyrolysis. *Prog Energy Combust* 2008;34(1):47–90.
- [66] Skreiberg A, Skreiberg O, Sandquist J, Sorum L. TGA and macro-TGA characterisation of biomass fuels and fuel mixtures. *Fuel* 2011;90(6):2182–97.
- [67] Sun LF, Chen JY, Negulescu LI, Moore MA, Collier BJ. Kinetics modeling of dynamic pyrolysis of bagasse fibers. *Bioresource Technol* 2011;102(2):1951–8.
- [68] Barneto AG, Carmona JA, Alfonso JEM, Serrano RS. Simulation of the thermogravimetry analysis of three non-wood pulps. *Bioresource Technol* 2010;101:3220–9.
- [69] Gonzalez JF, Ramiro A, Gonzalez-Garcia CM, Ganan J, Encinar JM, Sabio E, et al. Pyrolysis of almond shells. Energy applications of fractions. *Ind Eng Chem Res* 2005;44(9):3003–12.
- [70] Materazzi S. Mass spectrometry coupled to thermogravimetry (TG–MS) for evolved gas characterization: a review. *Appl Spectrosc Rev* 1998;33(3):189–218.
- [71] Peng YY, Wu SB. The structural and thermal characteristics of wheat straw hemicellulose. *J Anal Appl Pyrol* 2010;88(2):134–9.
- [72] Yang T, Lua AC. Characteristics of activated carbons prepared from pistachio-nut shells by physical activation. *J Colloid Interface Sci* 2003;267(2):408–17.